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APPLIED PHYSICS LETTERS **100**, 162901 (2012)

# Vacancy-driven ferromagnetism in ferroelectric $PbTiO_3$

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The possible origin of ferromagnetism in $PbTiO_3$ containing vacancies is investigated by performing first-principles calculations. We demonstrate that O and Ti vacancies both induce ferromagnetism but by different mechanisms: the ferromagnetism driven by the O vacancy originates from the spin-polarized $e_g$ state of the nearest Ti atom, whereas that driven by the Ti vacancy is due to the half-metallic $p_x$ state of the nearest O atom. The results presented here provide fundamental insights into the design of multiferroics in conventional ferroelectrics. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4704362]

Ferroelectric $PbTiO_3$ and its solid solutions, e.g., $Pb(Zr,Ti)O_3$, possess particularly large spontaneous polarizations and piezoelectric responses. Consequently, they are widely used in technological devices such as nonvolatile random access memories (FeRAMs), transducers, and electromechanical devices.[1,2] Conventional ferroelectrics, such as $PbTiO_3$ and $BaTiO_3$, are well-known to be non-magnetic materials, because the formal $d^0$ electron configuration (e.g., $Ti^{4+}$) in these ferroelectrics obviously contradicts with the partially filled $d$ states required for ferromagnetism.[3] In contrast, the existence of weak ferromagnetism was unexpectedly discovered in $PbTiO_3$ nanoparticles.[4] Experimental measurements suggest that vacancies included in $PbTiO_3$ may play a significant role in inducing ferromagnetism.[5,6] However, the origin of ferromagnetism has yet to be elucidated.

Materials that simultaneously exhibit ferroelectricity and ferromagnetism/antiferromagnetism in the same phase are known as multiferroics. Multiferroics have attracted considerable attention in recent years owing to the additional intriguing feature that the coexisted ferroic properties strongly coupled with each other, i.e., magnetoelectric (ME) coupling. Because the ME coupling enables ferroelectricity (ferromagnetism) to be controlled by applying a magnetic (electric) field, multiferroics have the potential to realize advanced technological devices, such as multiple-state memory elements and new functional sensors.[7–10] Defective ferroelectric $PbTiO_3$ that simultaneously exhibits ferromagnetism is one of the good candidates for multiferroics. For the use and applications as multiferroics, it is essential to reveal the detailed origin of ferromagnetism and the electronic-level mechanism.

This letter investigates which, if any, vacancies involves ferromagnetism and provide electronic-level insight into the origin of ferromagnetism in $PbTiO_3$, by performing first-principles density-functional theory (DFT) calculation. The results obtained here should be promising for materials design of multiferroics.

We perform first-principles spin-density-functional theory calculations implemented in the VASP code[11,12] using plane-wave basis sets with a cutoff energy of 500 eV. The electron-ion interaction is described by projector-augmented wave (PAW) potentials[13] explicitly including the Pb 5$d$, 6$s$, and 6$p$, the Ti 3$s$, 3$p$, 3$d$, and 4$s$, and the O 2$s$ and 2$p$ electrons in the valance states. A $5 \times 5 \times 5$ Monkhorst-Pack $k$-point mesh is used for the Brillouin zone integrations. For the simulation model, we employ a $2 \times 2 \times 2$ periodic supercell with 40 atoms in which two perovskite-unit-cells are arranged in each $x$, $y$, and $z$ direction.[14,15] We consider both [100]-polarized tetragonal $PbTiO_3$ in the ferroelectric (FE) phase and cubic $PbTiO_3$ in the paraelectric (PE) phase. A vacancy, denoted as $V_i$ ($i =$ Pb, Ti, O1, and O2) is introduced by removing one $i$ atom from the simulation supercell. Note that the oxygens O1 and O2, which are located in the [100] direction and the [010] or [001] direction relative to the Ti atom, respectively, are not equivalent to each other in the ferroelectric phase. The atomic structure is fully relaxed until the Hellmann-Feynman forces drop below 0.01 eV/Å.

Table I lists the magnetic moments $M$ of various vacancies in the tetragonal and cubic $PbTiO_3$. We find nonzero magnetic moments for the O1 and Ti vacancies in both the phases, i.e., emergence of ferromagnetism, whereas there is no magnetization for the Pb vacancy. The Ti vacancy induces a larger magnetic moment than the O1 vacancy. Moreover, the non-trivial difference in magnetic moments between the FE and PE phases indicates that the ferroelectricity strongly affects the ferromagnetism induced by the vacancies. This fact implies potential magnetoelectric coupling.

Figures 1(a) and 1(b) show the spatial distributions of the magnetization density around the O1 and Ti vacancies, respectively. For the O1 vacancy, the magnetization mainly appears around the $V_{O1}$ site and the nearest-neighbor Ti atoms. Magnetization is particularly localized around the Ti atom, which are strongly bonded with the O1 atom in a perfect crystal. For the Ti vacancy, on the other hand, the magnetization is localized at the neighboring O1 atom. It

TABLE I. Magnetic moment per vacancy $M$ (in $\mu_B$) of various vacancies in the tetragonal (FE) and cubic (PE) $PbTiO_3$.

| | $V_{O1}$ | $V_{O2}$ | $V_{Ti}$ | $V_{Pb}$ |
|---|---|---|---|---|
| Tetragonal (FE) | 0.488 | – | 1.633 | – |
| Cubic (PE) | 1.570 | ($=V_{O1}$) | 2.223 | – |

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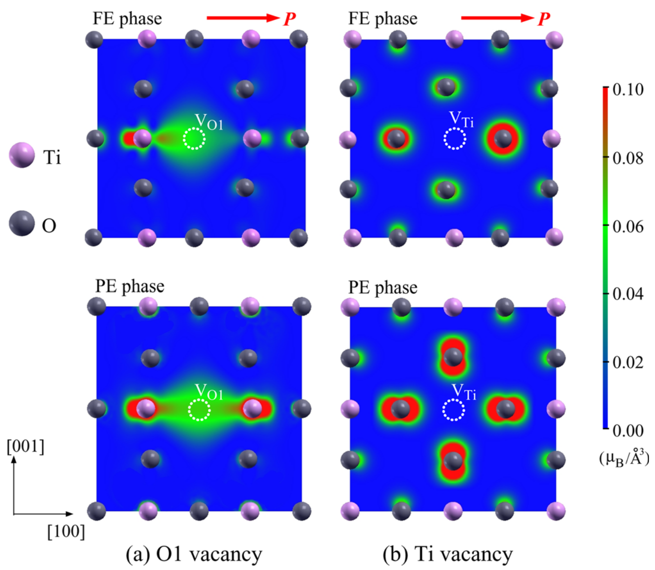


FIG. 1. Magnetization density distributions around (a) O1 vacancy and (b) Ti vacancy in the (010) plane. The top and bottom panels correspond to the FE and PE phases, respectively.

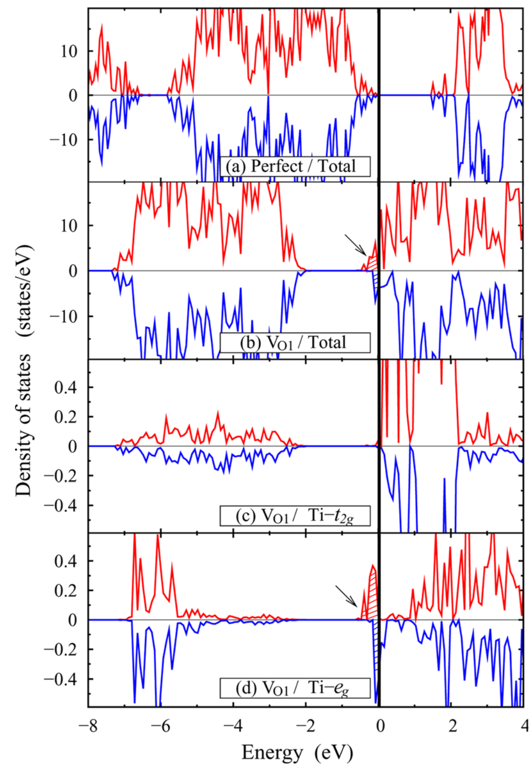


FIG. 2. Total electronic DOS for the (a) perfect and (b) O1-deficient tetragonal $PbTiO_3$. The projected DOS for (c) $t_{2g}$ and (d) $e_g$ states of the Ti atom nearest to $V_{O1}$. The red and blue lines, respectively, represent the majority and minority spins, and the solid vertical line indicates the Fermi level.

should be noted that in the FE phase, the magnetization is mainly localized around only one Ti (or O1) atom nearest to $V_{O1}$ (or $V_{Ti}$), whereas both the two neighboring Ti (or six neighboring O1) atoms carry a large magnetization in the PE phase. This anisotropy in the magnetization density distribution should be due to a ferroelectric displacement along [100]. Thus, the number of atoms carrying the magnetization causes the different magnetic moments of the FE and PE phases.

To give more insight into the origin of ferromagnetism induced by the vacancies, we investigated the electronic density of states (DOS). Total DOS for the perfect and O1-deficient tetragonal $PbTiO_3$ are shown in Figs. 2(a) and 2(b), respectively. Perfect $PbTiO_3$ behaves as an insulator with a band gap energy of 1.6 eV. This value agrees well with that found in a previous study[16] but is smaller than the experimental value of 3.5 eV (Ref. 17): this discrepancy is a well-known problem within the framework of the density functional theory. The O1 vacancy causes the Fermi level to shift up and forms a new state near the bottom of the conduction band, indicating an *n*-type behavior. The DOS just below the Fermi level asymmetrically differs between the majority and minoristy spins. Thus, this spin-polarized state contributes to ferromagnetism. Figures 2(c) and 2(d) show the projected DOS for the 3*d* states of the Ti atom nearest to $V_{O1}$, where the magnetization is mainly concentrated. Here, the $O_h$-type crystal field in the perovskite structure splits the 3*d* orbitals of the Ti atom into two $e_g(d_{x^2-y^2}$ and $d_{z^2})$ and $t_{2g}(d_{xy}, d_{yz},$ and $d_{zx})$ states, which distribute toward the six neighboring O atoms and toward the four neighboring Pb atoms, respectively. The $e_g$ orbital forms the spin-polarized state just below the Fermi level, suggesting a partially filled 3*d* state on the Ti atom, whereas the $t_{2g}$ orbital does not contribute to the state at all. In addition, the magnetization density distribution localized between the Ti and $V_{O1}$, as shown in Fig. 1(a), corresponds well to the $e_g$ orbital. Therefore, the $e_g$ states of the Ti atom adjacent to $V_{O1}$ makes a dominant contribution to ferromagnetism induced by the O1 vacancy. It should be noted that the Ti-$e_g$ orbital hybridizes with the O1-$p_x$ orbital by forming a $p$-$d\sigma$ bond in perfect $PbTiO_3$. Thus, the loss of the $\sigma$ bond by the O1 vacancy leads to the partially filled spin-polarized 3*d* state. This result agrees well with the experimental fact that $Ti^{4+}$ is reduced to $Ti^{3+}$ in oxygen-deficient octahedra by charge compensation.[18]

For the Ti vacancy, on the other hand, the nature of the induced ferromagnetism differs from that of the O1 vacancy: Figures 3(a) and 3(b) show the total DOS for perfect and Ti-deficient tetragonal $PbTiO_3$, respectively. The Fermi level for the Ti vacancy shifts down slightly relative to that of the perfect $PbTiO_3$. Consequently, the DOS cross the Fermi energy. Interestingly, the majority spin bands for the Ti vacancy are fully occupied and exhibits insulating characteristics with a band gap. On the other hand, the minority spin DOS crosses the Fermi level and exhibits a conductive character. This indicates that the Ti vacancy shows a half-metallic behavior. The small portion of the minority spin DOS appearing just above the Fermi level indicates that there are more majority spins than that of the minority spins, i.e., it is a spin-polarized state. Figures 3(c) and 3(d) plot the projected DOS for the $p_x$ and $p_y$ ($= p_z$ for the tetragonal symmetry) states of the O1 atom nearest to $V_{Ti}$, respectively. All the 2*p* states of the O1 atom are polarized because the DOS of the majority and minority spins are asymmetric. However, the $p_x$ state exhibits the fully occupied majority spin and the partially filled minority spin states, whereas both the spins are almost fully occupied in the $p_y$ and $p_z$ states. This result suggests that the $p_x$ state of the neighboring O1 atom to $V_{Ti}$ mainly contributes to the magnetization induced by the Ti vacancy. As mentioned above, the O1-$p_x$ orbital forms a $\sigma$

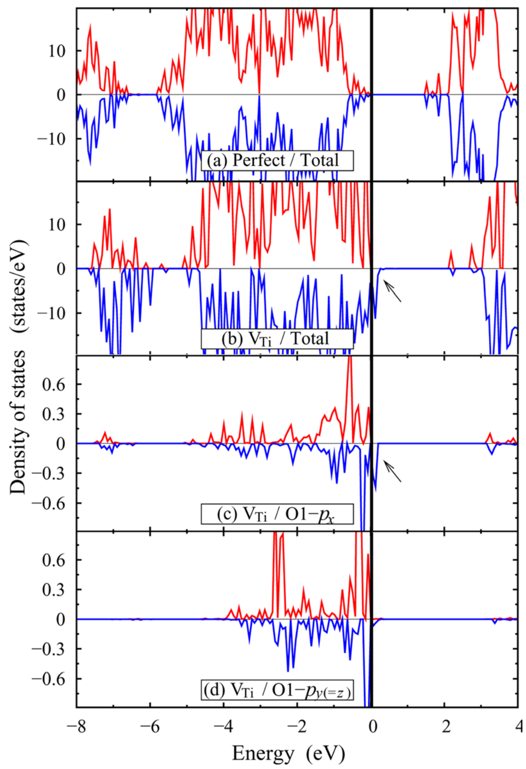


FIG. 3. Total electronic DOS for the (a) perfect and (b) Ti-deficient tetragonal $PbTiO_3$. The projected DOS for (c) $p_x$ and (d) $p_y(=p_z)$ states of the O1 atom nearest to $V_{Ti}$. The red and blue lines, respectively, represent the majority and minority spins, and the solid vertical line indicates the Fermi level.

bond in perfect $PbTiO_3$ through hybridization with the Ti-$e_g$ orbital. Hence, the loss of this bond due to the Ti vacancy leads to the half-filled spin-polarized $p_x$ state. A similar trend is found for the same vacancy in $BaTiO_3$.[14]

The oxygen vacancy is energetically more stable than the Ti vacancy,[19,20] suggesting that in practical situations, the oxygen vacancy has a larger population than other vacancies. Thus, the O1 vacancy is the main source of the ferromagnetism emerging in $PbTiO_3$. This agrees well with the experimental fact that $PbTiO_3$ annealed in air exhibits a substantially smaller magnetic moment than that annealed in vacuum.[5]

Although Cao *et al*. reported vacancy-induced magnetism in $BaTiO_3$,[14] there are three non-trivial differences between $PbTiO_3$ and $BaTiO_3$: (i) The O2 as well as O1 vacancies drive magnetism in $BaTiO_3$. (ii) There is almost no difference in the magnetic moments between FE and PE $BaTiO_3$ by the O1 vacancy (1.27 and 1.23 $\mu_B$, respectively), while the difference is more pronounced in $PbTiO_3$ (see Table I). This is because the ferroelectric distortion of FE $PbTiO_3$ is considerably large, whereas that of FE $BaTiO_3$ is relatively smaller and much close to the PE structure due to the different bonding nature.[21] (iii) The $t_{2g}$ state mainly contributes to magnetism by the O1 vacancy in $BaTiO_3$, while the $e_g$ state does for $PbTiO_3$.

In summary, the origin of ferromagnetism emerging in $PbTiO_3$ with vacancies, and its electronic-level mechanism were investigated by performing first-principles DFT calculations. We demonstrated that O and Ti vacancies both induce ferromagnetism but by different mechanisms: the ferromagnetism induced by the O vacancy originates from the spin-polarized $e_g$ state of the nearest Ti atom, whereas that driven by the Ti vacancy is due to the half-metallic $p_x$ state of the O atom nearest to the Ti vacancy. The results presented here provide fundamental insights for the future design of multiferroic materials by conventional ferroelectrics.

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